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(54) **METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES**
VERFAHREN ZUR HERSTELLUNG VON PARTIKELN AUS NANO-DIMENSION MATERIAL
PROCEDES DE PREPARATION DE PARTICULES DE MATIERE DE NANO-TAILLE

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Description

[0001] The present invention relates to the methods for the preparation of nanosized material particles, ("Nanomaterials" in connection with the present invention comprise transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 - 5 nm.) Nanomaterials are prepared from the corresponding precursors i.e. the corresponding metal salts or alkoxides by suitable chemical reactions, e.g. reduction, hydrolysis and exchange processes under mild conditions.

[0002] There are known methods to prepare clusters or fine colloids from said nanomaterials which are dispersed in different suitable solutions. Appropriate liquid media enable the production of different preparations, which may be used as thin films on various supports.

[0003] There are known several methods for the preparation of ultrathin films of metal particles on solid supports, e.g. ion implantation (M.Che. C.O. Bennet, Adv. Catal. 1989, 36, 55); organometallic chemical vapor deposition (A. Sherman, Chemical Vapor Deposition for Microelectronics, Principles, Technology and Application, Noyes Publications; Park Ridge, N.J. 1987; and N.H. Dryden et al., Chem. Mater. 1991, 3, 677); metal deposition from colloidal solution (G.Schmid, Chem. Rev. 1992, 92, 1709); reductive metal deposition from aqueous salt solution (I.Coulthard, et al., Langmuir 1993, 9, 3441.); photodecomposition of metal complexes in thin films (R.Krasnasky et al. Langmuir, 1991, 7, 2881); and photo-reductive deposition from Pd(II) complexes in solution (K. Kondo et al., Chem. Lett. 1992, 999). Other techniques are based on the film formation of noble metal loaded block copolymers (Y.NgCheongChen et al., Chem.Mater. 1992, 4, 24; and J.P.Spatz, et al., Adv. Mater. 1995, 7, 731.); on the Langmuir-Blodgett (LB) transfer of monolayers or surfactant stabilized metal colloids (F.S. Meldrum et al., Langmuir 1994, 10, 2035; and F.S. Meldrum et al., Chem. Mater. 1995, 7, 1112); and on thermal decomposition of LB films of zero valent palladium complexes (E. Maasen et al., Langmuir 1996, 12, 5601).

[0004] At present the microelectronic and some related industries, mainly continue to use the vapor deposition method. The "Wet" method, which is a method of film deposition from solutions, provides a good challenge for the industry since it does not require high temperatures and pressures or high vacuum and enables to vary the properties of the nano compositions to a large extent.

[0005] During the last decade, the number of scientific works devoted to the synthesis of nanomaterials in solutions has significantly increased. Certain practical results were reported. Thus, for example G. Schmid (see above) demonstrated that the pellets which consist of ligand stabilized golden clusters (derived from a liquid) may be regarded as tunnelling resonance resistors and, additionally, as cellular automates. The density of electronic switches, compared with common semiconductors increased in another example to a factor of 10^5 - 10^9 . Another paper (T. Yamamoto, in Macromolecular Complexes, Ed. by Bishun Tsuchida, VCH, 1993, 380-395.) informed about the preparation of electrically conducting polymer compositions by using organosols of metal sulfides. The polymer-composite films not only show good electrical conductivity but were also controlled to p- or n-type conductors.

[0006] The realization of quantum dots, of uniform size and structure opens the door to multiple switches. This enables the manufacture of new generations of computers with extremely high capacities. The manufacture of novel minilasers, based on quantizing particles, will most probably lead to optoelectronic switches, operated simultaneously by photons and electrons. Nanometal coatings may be effectively used, e.g. as film catalysts (for instance in the processes of electrodeless metal deposition); and as modifiers of mechanical properties of different materials.

[0007] However, all said conventional methods are not satisfactory in the preparation of coatings comprising nanomaterial particles, as they are rather complicated, expensive or do not yield the particles having the desired size.

[0008] It has thus been desirable to find a method which would overcome said disadvantages, i.e. should not be complicated, not be too expensive and yield nanomaterial particles having the desired size.

[0009] It is well known that water which appears to be a key factor which governs the association of surfactants in different solvents, functions not only as an inert solvent but plays a significant part in the mechanism of chemical processes. (Gartl et al. Coll. & Interface Sci. 178 (1996) p. 60-68). When describing the state of water in relation to any surface a distinction is usually made between "bulk" and "bound" water. It is assumed that "bulk" or free water has physico-chemical properties which are not very different from those of pure water. "Bound" water may be defined by the operational definitions which refer to the water detected by a certain technique.

[0010] According to the method utilized by Senatra (D. Senatra et al. Can. J. of Phys. 68 (1990) p. 1041), in which the endothermic scanning mode was applied and the peaks representing various states of water were identified and analyzed, it was shown that "free" water melts at 0°C, "interfacial bound" water melts at -10°C, and non-freezing water which is the most strongly bound part of bound water has no peaks on thermograms up to -100°C.

[0011] It has been found that the state of the water is strictly correlated with the size of the particles. Particles which have a diameter of less than 5 nm are synthesized in systems which comprise only strongly bound water (non freezing water according to subzero differential scanning Calorimetry DSC).

[0012] In developing the method according to the present invention it has been considered:

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- a. producing the water-organic-surfactant organized solutions (complex liquids) comprising nanosized particles in particular having a diameter of 1 - 5 nm which are useful for the particle preparation;
- b. regulating the water content in such a manner that the whole water will be strongly bound to the surfactant (non-freezing) in the system, thus enabling to provide nano particles which have a diameter of less than 5 nm;
- c. the regulation of the solution structures which enables the regulation of the morphology of the particles;
- d. the variation of the chemical composition and concentration of nano-precursors (and of the complementary reactants), which enables the control of the particle size distributions (PSD) and of the thickness of the protecting shells;
- e. using different polymers which enable the production of films having different adhesion properties, by the deep coating method; and
- f. the control of the viscosity and of the velocity of the solutions which lead to different film thicknesses;

[0013] The optimization of the above-mentioned factors (which should operate simultaneously) should lead to the production of the coating having the desired properties.

[0014] The present invention thus consists in a method for the production of nanosized particles having an average diameter of less than 6nm, said nanosized particles being selected from transition metals, transition metal alloys, metal oxides and ceramic compositions,

in which said nanosized particles are synthesized in a complex liquid which is an organised water-organic surfactant solution and wherein the water in the solution is non-freezing water

from precursors selected from metal salts and alkoxides

said nanosized particles being synthesised by a chemical reaction under mild conditions and preparing from said nanosized particles fine colloids dispersed in a polymer solution.

[0015] The nanomaterial particles have advantageously a diameter of 1-6 nm.

[0016] The water in the solution is non-freezing water as determined by low temperature differential scanning calorimetry

[0017] The suitable chemical reaction may be selected, for example, among reduction, hydrolysis and exchange processes.

[0018] Mild conditions in connection with the present invention are suitably atmospheric pressure and a temperature range of room temperature to 70°C.

[0019] Suitable solutions may be selected among microemulsions and liquid crystalline media.

[0020] Suitable organic solvents may be, e.g. selected among suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); ethers (ethylether); etc.

[0021] The appropriate liquid media enable the preparation of different self assemblies of nanomaterials and subsequently the use of them as thin films on various supports.

[0022] Suitable surfactants are, for example,:

Quaternary ammonium salts, e.g. trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB), etc.; sodium bis-(2-ethyl-hexyl) - sulfosuccinate; polyethoxyethylene-10-oleyl ether (Bij 98; etc.

Oxide precursors may be, e.g. alkoxides:

tetraethyl orthosilicate (TEOS); tetramethoxy silane (TMOS); Al, Zr isopropoxides, etc;

Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride; etc. Metal precursors may be, e.g. transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt, e.g. FeCl₃, K₂PdCl₄, K₂PtCl₄ and CuCl₂.

[0023] The polymers may be selected, e.g. from polyethylene oxide (PEO), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), etc.

[0024] Suitable reducing agents are, for example, sodium formate; hydrogen; certain alcohols (methanol, ethanol, isopropylalcohol); etc.

[0025] The method according to the present invention can direct the morphology, dimension and homogeneity of the size distributions of the small colloids (and clusters) and also their self assembling.

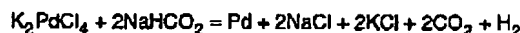
Example 1

[0026] A Pd colloidal dispersion was prepared from a solution containing 12% wt of hydrated trioctylmethylammonium chloride (aliquat 336) which corresponds to water/aliquat molar ratio = 3.06. Sub-zero DSC analysis did not reveal any

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peak which belongs to interfacial (-10°C) and free water (0°C) in the precursor solution.

[0027] Potassium tetrachloropalladate (K_2PdCl_4) (326mg) was solubilized in a 5 ml aliquat-dichloroethane-water mixture. Sodium formate (NaHCO_2) (0.22 gr) was poured onto the mixture under argon. The reaction was carried out in accordance with the following formula:



[0028] The reaction was carried out at 75°C . In the course of the reaction, the orange color gradually changed to a dark brown color. The reaction was stopped after 1 hour and the dichloroethane was evaporated from the reaction mixture. The waxy residue obtained, was washed, in order to remove the inorganic salts, with deionized water and dried at 30 torr and 60°C .

[0029] Electron diffraction data revealed a face centered-cubic (fcc) Pd phase, while Transmission Electron Microscopy (TEM) analysis showed round particles having a mean diameter of 1.8 nm.

[0030] The nanometal prepared was redispersed in 40 ml of dichloro-ethane containing 30% of a v/v Polyvinyl alcohol (PVA). The viscosity of the solution was 40 cps.

[0031] The surface of a glass plate was thoroughly cleaned with hot water, methyl alcohol and diethyl ether. A coating was prepared by drawing with the velocity of 8 mm/sec. The bright orange transparent film obtained had a magnitude of electrical conductivity $10^{-6} \Omega^{-1}\text{cm}^{-1}$.

Example 2

[0032] 1.25 g of a commercially available nonionic surfactant Brij-96 (poly- ethoxyethylene- 10- oleyl ether $\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ (PEO) was added to a mixture of 4 ml of hexane and 1.18 g of t-butanol. 1 ml of a 0.025M solution of FeCl_3 in 0.01 HCl was then poured on the mixture. The mixture was homogenized by Vortex and it then looked like a homogenous solution. The sub-zero DSC analysis did not reveal any peak which belong to freezing water. After an ageing process at 40°C in the course of 48 hr, TEM and small angle X-ray scattering (SAXS) there were visualized particles having a mean diameter of 3.5 nm and 10% degree of polydispersion. Photoelectronic Spectroscopy (XPS) analysis indicated FeOOH formation. The microemulsion was concentrated by evaporation at 35°C and 60 torr and the wax residue obtained was redispersed in 10 ml of Polyethylene glycol (PEG). The viscosity of the solution was 9.3 cps. A coating was prepared by drawing with the velocity of 12 mm/sec. Coming glass plates were soaked in ethanol solutions in the course of 24 hr rinsed with distilled water under sonication, then immersed in ethanol and dried at 105°C for 8 hr. A film was formed on the glass plate by spreading of the solution. After a film heat treatment at 45°C the film was not cracked or destroyed. Scanning electron microscopy (SEM) of the coating (removed from the support) did not show any growth of the particles.

Example 3

[0033] 0.5 g of commercially available surfactant didodecylammonium bromide (DDAB) containing 6% of water was added to 7 ml of toluene, and stirred with shaking to form an inverse micellar solution. Thereafter 0.025 g of K_2PtCl_6 and 1.2 ml of tetraethylorthosilicate (TEOS) were added to the solution obtained, which was then stirred until the salt was fully solubilized. Then NaBH_4 was poured into the salt precursor solution with rapid stirring in an argon atmosphere so that the $[\text{BH}_4] : [\text{Pt}^{4+}]$ relation was 4:1. The solution gradually turned to dark brown. The pH of the solution was adjusted to 6.5 by the addition of an organic buffer in ethanol. The solution was aged at room temperature during 3 days previous to film formation by deep coating. According to sub-zero DSC data, the system did not contain any freezing water. The viscosity of the solution was 7.2 cps. A coating was prepared by drawing with the velocity of 12 mm/sec.

[0034] Glass substrates were cleaned in the same manner as described in Examples 1 and 2. In order to enhance the adhesion of the film to the glass, cleaned and dried glass supports were immersed in a 0.5% ethanol solution of triaminopropyltriethoxysilane, rinsed with dichloromethane and ethanol and baked in an oven at 120°C for 2 hr. SAXS, TEM, XPS and SEM analyses were indicative of nanosize (3-5 nm) Pt (partially oxidized on the surface) particles embedded in the silica matrix. Low temperature nitrogen adsorption of the separated film dried at 100°C in the course of 3 hr showed 37% film porosity having a mean pore diameter of 35\AA . Thermo treatment of the film at 450°C for 1 hr did not change the pore characteristics of the film. Such prepared substrates were suitable in electroless Ni plating. A typical plating solution contained 0.105 mol of $\text{L}^{-1} \text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.195mol of $\text{L}^{-1} \text{H}_2\text{PO}_2$.

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Claims

1. A method for the production of nanosized particles having an average diameter of less than 8nm, said nanosized particles being selected from transition metals, transition metal alloys, metal oxides and ceramic compositions, in which said nanosized particles are synthesized in a complex liquid which is an organised water-organic-surfactant solution and wherein the water in the solution is non-freezing water from precursors selected from metal salts and alkoxides said nanosized particles being synthesised by a chemical reaction under mild conditions and preparing from said nanosized particles fine colloids dispersed in a polymer solution.
2. A method according to claim 1 in which the nanosized particles have an average diameter of between 1 and 6nm.
3. A method according to Claim 1 or 2, wherein the nanomaterial particles have an average diameter of less than 5nm, preferably 1-5 nm.
4. A method according to any of Claims 1 to 3, wherein the mild conditions are atmospheric pressure and a temperature range of room temperature to 70°C.
5. A method according to any of Claims 1 to 4, wherein the chemical reaction is selected among a hydrolysis, reduction and exchange process.
6. A method according to any of Claims 1 to 5, wherein the complex liquids are selected among microemulsions and liquid crystalline media.
7. A method according to any of Claims 1 to 6, wherein the organic solvent is selected among suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); and ethers (ethylether).
8. A method according to any of Claims 1 to 7, wherein the surfactants are selected among trioctylmethyl ammonium chloride (allquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB); sodium bis-(2-ethyl-hexyl)-sulfosuccinate; and poly-ethoxyethylene-10-oleyl ether.
9. A method according to any of Claims 1 to 6, wherein metal oxides and precursors are selected among tetraethyl orthosilicate (TEOS); tetramethoxy silane (TMOS); Al, Zr isopropoxides; Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride and transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt.
10. A method according to any of Claims 1 to 9, wherein the polymers are selected among polyethylene oxide (PEO); polyvinyl chloride (PVC); polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).
11. A method according to any of Claims 5 to 10, wherein the nanosized particles are synthesised by reduction and the reducing agent is selected among sodium formate; hydrogen; and certain alcohols (methanol, ethanol, isopropylalcohol).

Patentansprüche

1. Verfahren zur Herstellung von Partikeln in Nanogröße mit einem durchschnittlichen Durchmesser von weniger als 8 nm, wobei die Partikel in Nanogröße aus Übergangsmetallen, Übergangsmetallegierungen, Metalloxiden und/oder keramischen Zusammensetzungen ausgewählt werden, bei welchem die Partikel in Nanogröße in einer Komplex-Flüssigkeit, die eine organisierte Wasser-organischoberflächenaktiver Stoff-Lösung ist und in welcher das Wasser in der Lösung nicht-gefrierendes Wasser ist, aus Zwischenprodukten synthetisiert werden, die aus Metallsalzen und/oder Alkoxiden ausgewählt werden, die Partikel in Nanogröße durch eine chemische Reaktion unter sanften Bedingungen synthetisiert werden und aus den Partikeln in Nanogröße Feinkolloide erzeugt werden, die in einer Polymerlösung dispergiert sind.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Partikel in Nanogröße einen durchschnittlichen Durchmesser zwischen 1 und 6 nm besitzen.

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3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Nanopartikel einen durchschnittlichen Durchmesser von weniger als 5 nm, vorzugsweise zwischen 1 und 5 nm besitzen.
- 5 4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die sanften Bedingungen Atmosphärendruck und ein Temperaturbereich von Raumtemperatur bis 70°C eind.
5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die chemische Reaktion eine Hydrolyse, eine Reduktion und/oder ein Austauschverfahren ist.
- 10 6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Komplexflüssigkeiten Mikroemulsionen und/oder Flüssigkristallmedien eind.
7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das organische Lösungsmittel aus geeigneten Kohlenwasserstoffen (Oktan, Dekan, Dodekan), Chlorkohlenwasserstoffen (1,2 - Dichlorethan) und/oder Ether (Ethylether) ausgewählt ist.
- 15 8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß die oberflächenaktiven Stoffe aus Trioctylmethyl-Ammoniumchlorid (Allquat 336), Dioctyldimethyl-Ammoniumbromid (DDAB), Cetyltrimethyl-Ammoniumchlorid (CTAB), Natriumbis-(2-Ethyl-Hexyl)-Sulfosukzinat, und/oder Poly-Eoxyethylen-10-Oleyl-Ether ausgewählt sind.
- 20 9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Metalloxyde und Zwischenprodukte aus Tetraethyl-Orthosilikat (TEOS), Tetramethoxyellon (TMOS), Al-, Zr-Isopropoxyden, Fe-, Mg- und Al-Chloriden, Al- und Mg-Azetaten, Na- und K-Orthosilikaten, Zr-Oxychlorid und/oder Übergangsmetallsalzen aus Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir und Pt ausgewählt sind.
- 25 10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß die Polymere aus Polyethylenoxid (PEO), Polyvinylchlorid (PVC), Polyvinylalkohol (PVA) und/oder Polymethyl-Methacrylat (PMMA) ausgewählt sind.
- 30 11. Verfahren nach einem der Ansprüche 5 bis 10, dadurch gekennzeichnet, daß die Partikel in Nanogröße durch Reduktion synthetisiert werden und das Reduzierungsmittel aus Natriumformiat, Wasserstoff und/oder bestimmte Alkohole (Methanol, Ethanol, Isopropylalkohol) ausgewählt ist.

35 Revendications

1. Procédé pour la production de particules de nano-taille ayant un diamètre moyen inférieur à 6 nm, lesdites particules de nano-taille étant choisies parmi les métaux de transition, alliages de métaux de transition, oxydes métalliques et compositions céramiques,
- 40 dans laquelle lesdites particules de nano-taille sont synthétisées dans un liquide complexe, qui est une solution d'eau-organique-de surfactants organisée et dans laquelle l'eau dans la solution est une eau incongelable issues de précurseurs choisis parmi des sels et des alcoxydes métalliques lesdites particules de nano-taille étant synthétisées par une réaction chimique dans des conditions douces et la préparation à partir de ces particules de nano-taille, de colloïdes fins dispersés dans une solution polymère.
- 45 2. Procédé selon la revendication 1, dans laquelle les particules de nano-taille ont un diamètre moyen entre 1 et 6 nm.
3. Procédé selon la revendication 1 ou 2, dans laquelle les particules de matière de nano-taille ont un diamètre moyen inférieur à 5 nm, préférablement de 1 à 5 nm.
- 50 4. Procédé selon l'une quelconque des revendications 1 à 3, dans laquelle les conditions douces sont la pression atmosphérique et une plage de température de température ambiante jusqu'à 70 °C.
- 55 5. Procédé selon l'une quelconque des revendications 1 à 4, dans laquelle la réaction chimique est choisie parmi un procédé d'hydrolyse, de réduction ou d'échange.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans laquelle les liquides complexes sont choisis parmi

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les microémulsions et les milieux cristallins liquides.

- 5 7. Procédé selon l'une quelconque des revendications 1 à 6, dans laquelle le solvant organique est choisi parmi des hydrocarbures appropriés (octane, décane, dodécane); hydrocarbures chlorés (1,2-dichloro-éthane); et éthers (éthyléther).
- 10 8. Procédé selon l'une quelconque des revendications 1 à 7, dans laquelle les surfactants sont choisis parmi les chlorure de trioctylmethyl ammonium (aliquat 336), bromure de dioctyldiméthylammonium (DDAB), chlorure de cetyltriméthylammonium (CTAB); bis-(2-éthyl-hexyl)-sulfosuccinate de sodium; et poly-éthoxyéthylène-10-oléyl éther.
- 15 9. Procédé selon l'une quelconque des revendications 1 à 6, dans laquelle les oxydes métalliques et les précurseurs sont choisis parmi les orthosilicates de tétraéthyle (TROE); tétraméthoxy silane (TMOS); iso-propoxydes de Al, Zr; chlorures de Fe, Mg et Al; acétates de Al et Mg; orthosilicates de Na et K; oxychlorure de Zr et sels de métaux de transition de Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir et Pt.
- 20 10. Procédé selon l'une quelconque des revendications 1 à 9, dans laquelle les polymères sont choisis parmi les oxyde de polyéthylène (PEO); chlorure de polyvinyle (PVC); alcool de polyvinyle (PVA); et méthacrylate de polyméthyle (PMMA).
- 25 11. Procédé selon l'une quelconque des revendications 5 à 10, dans laquelle les particules de nano-taille sont synthétisées par réduction et l'agent réducteur est choisi parmi les formate de sodium; hydrogène; et certains alcools (méthanol, éthanol, alcool isopropylique).
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